

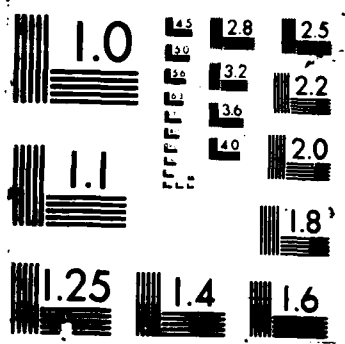
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HIGH-MOLECULAR COMPOUNDS
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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ѐ in Russian, transliterate as yě or ě.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	\sinh^{-1}
cos	cos	ch	cosh	arc ch	\cosh^{-1}
tg	tan	th	tanh	arc th	\tanh^{-1}
ctg	cot	cth	coth	arc cth	\coth^{-1}
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian English

rot curl
lg log

GRAPHICS DISCLAIMER

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STUDY OF THE AFFECT OF THE ADDITION OF ACETOPHENONE AND TOLUENE ON
PROPERTIES OF COPOLYMERS OF METHYLMETHACRYLIC AND METHYLACRYLIC IN
EMULSIONS BY THE METHOD OF NUCLEAR MAGNETIC RESONANCE

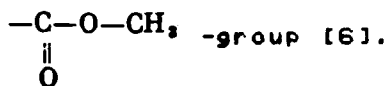
L. V. Ivanova, V. I. Sheychenko, P. I. Zubov, V. I. Yeliseyeva, N. I.
Savaya

Earlier [1,2] it was shown that 33% emulsions of copolymers of
methylnmethacrylic (MA) with methylacrylic (MA) with the addition of
acetophenone and other organic liquids in the amount of 10-40% acquire
the property of sharply pronounced thixotropy, which is characterized
by the reduction of viscosity by 5 orders in a narrow interval of
stresses. Interpretation of this phenomenon is deserving of attention.
In particular, it is interesting to discover whether it is possible to
examine the onset of thixotropic properties as the result of the
combination of the particles of a polymer with an additive, which
occurs in a dispersion aqueous medium. The good solubility of
copolymers in liquid-additives, established from data of light
scattering [3], is a certain indirect indication of a possibility of
such combination. However, in order to obtain direct evidence other
methods are required, in connection with which we selected the method

Concl¹¹⁶ of NMR. The results presented here of a study of the indicated systems by the NMR method are evidence of the qualitative change of particles of the dispersion due to the affect of the organic additive, which can be a consequence of the combination of particles with organic liquid in aqueous dispersion medium. *(Puss...)*

The NMR measurements were carried out with the S-60 spectrometer at a frequency of 60 MHz. Figure 1 shows NMR spectra for emulsions of copolymers of MMA and MA without additive and with additive of acetophenone 40 parts by weight per 100 parts by weight of emulsion. Toluene, introduced into the emulsion during synthesis, is contained in all samples at the rate of 17% of the original emulsion. The spectrum of the emulsion 80 MMA : 20 MA (Fig. 1, spectrum 1) does not contain any lines of the copolymer, and the resulting lines are respectively the lines: a-C₆H₅ of the toluene ring, b-protons of water and d-CH₃-group of toluene. The absence of signals from the copolymer, which contains 80% MMA, is easily interpreted as a consequence of the stability of the polymer, which is retained in view of the fact that the polymer is not soluble to individual molecules, and is represented form of dispersed particles. Considering that the amplitude of the absorption signal is directly proportional to the square route of the time of spin-spin relaxation T₂ [4] and that the time T₂ is greatly reduced with an increase of the stability of the polymer system [5], for such sufficiently stable systems as plastified 50% toluene the copolymer 80 MMA : 20MA (Fig. 2, curve 1) we see that the signal of residence is located below the limit of sensitivity of the spectrometer

and therefore does not appear on the spectrum. With an increase of flexibility of the polymer by increasing the content of the elastic component MA (Fig. 1, spectrum 2) among other signals of the spectrum one can also observe a signal of the polymer in the form of a line from



$$v \approx N\sqrt{T_2/T_1}$$

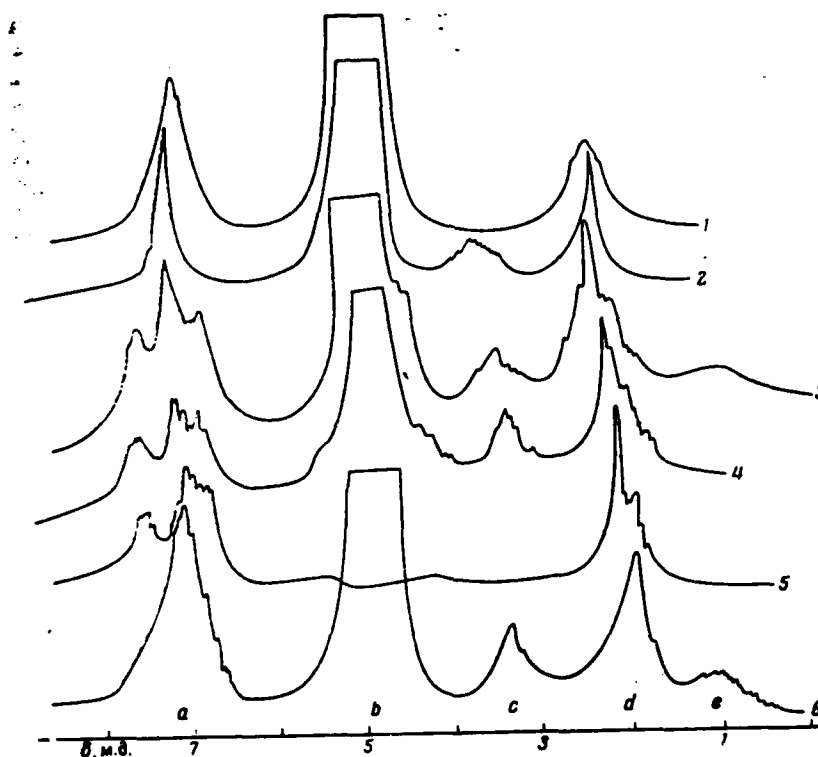


Fig. 1. NMR spectra of aqueous emulsions of copolymers MMA : MA with additives of toluene and acetophenone, parts by weight:

(1) (80 MMA : 20 MA) is 33, toluene is 17, water is 50; (2) (10 MMA : 90 MA) is 33, toluene is 17, water is 50; (3) (80 MMA : 20 MA) is 33, toluene is 17, water is 50; acetophenone is 40; (4) (10 MMA : 90 MA) is 33, toluene is 17, water is 50, acetophenone is 40; (5) Toluene: acetophenone = 2 : 5; (6) (80 MMA : 20 MA) is 33, toluene is 57, water is 50; a-e, see text.

The signal δ on the spectra 2, 3, 4, 6 of Fig. 1, which is characterized by a shift of the order 3.4-3.7 dose rate (relative to tetramethylsilane), is a signal of a the indicated group, which, as is known, occurs in the marked off region, changing its position within limits of the interval of chemical shifts 3.1-3.7 dose rate in relationship to the chemical nature of the solvent, which forms the external medium for polymer molecules [6].

Spectrum 5 in Fig. 1 is a mixture of toluene and acetophenone in the ratio 2 : 5. The spectrum contains characteristic signals of the benzene ring and the methyl group of toluene and acetophenone and does not contain signals in the region δ as in 2, 3, 4, 6 (Fig. 1). Consequently, the signal δ , not being a result of additional shiftings of the chemical shift of the groups C_6H_5 and CH_3 of toluene and acetophenone due to the affect of the second component, actually is a signal of the ester methyl group of the copolymer. The appearance of the signal of a copolymer in the spectrum 3 of Fig. 1 indicates plastification of the copolymer by acetophenone in the aqueous medium.

Such plastification of particles of the polymer by an organic liquid, which leads to the appearance of the MMR signal, occurs during introduction into the emulsion of an additional quantity of toluene: 40 parts by weight for 100 parts by weight of emulsion. In Figure 1 (spectrum 6) we indicate the spectrum of the emulsion of the polymer 80 MMA : 20 MA, which contain 33 parts by weight of polymer and 50 parts by weight of water 57 parts by weight of toluene, where in the regions

s there also occurs a signal of the ester methyl group of the copolymer. In this spectrum in the region ϵ , as in the spectrum 3 of Fig. 1 a signal of the methyl group is evident, which is in the carbon atom of the polymer chain, with a shift on the order of 1 dose rate [7].

The spectrum 2 and 4 in Fig. 1 pertain to 33% emulsion of copolymer 10 MMA : 90 MA, which consists basically of the elastic component, polymethacrylate, and which therefore manifests the signal ϵ in the spectrum with initial plastification by toluene (spectrum 2). With additional plastification of the emulsion by acetophenone (40 parts by weight for 100 parts by weight of emulsion) this signal narrows [8] from the half width of 0.5 m.d. to 0.25 m.d. (spectrum 4 in Fig. 1).

In view of the definite relationship of the appearance or absence of NMR signals of copolymers to the degree of their elasticity or rigidity it is interesting to compare these data with mechanical properties of copolymers MMA and MA, which contain a corresponding amount of plastifier. The mechanical properties of the examined polymer systems were studied by the method of the growth of deformation of the shift with constant stress [9], and results are presented in Fig. 2. Curve 1, located near the axis of the abscissa, indicates the formability of plastified 50% toluene of the copolymer 80 MMA : 20 MA, which, as one can see, is quite small and corresponds to such low mobility of molecules, at which the NMR signal is not observed.

Introduction of acetophenone in the ratio, which occurs in the emulsion (40 parts by weight to 33 parts by weight of copolymer) develops a very high deformability of the system, which is represented by curve 4 (Fig. 2), located near the axis of the ordinate. The mobility of molecules with this degree of plastification determines the occurrence of a signal s in spectrum 3 of Fig. 1.

For the other copolymer, 10 MMA : 90 MA, the NMR signal (s in the spectra 2 and 4 of Fig. 1) occurs in both cases of plastification: 50% toluene and 50% toluene + 120% acetophenone. As is evident from Fig. 2, the less plastified sample is represented by curve 3, located near the curve 4, and also indicates sufficiently high deformability. The development of a shift in time for 10 MMA : 90 MA, which contains 50% toluene and 120% acetophenone is designated in Fig. 2 by the same curve 4. The deformation characteristics of both systems (10 MMA : 90 MA and 80 MMA : 20 MA) with different number of plastifiers, possibly differ slightly from one another, however the difference is found within the range of the spread of data which is caused by instability of the system during the experiment because of evaporation of the plastifier, in spite of the evaporation protection used [9]. The role of evaporation of plastifier and protection from it during the experiment is evident from the fact that without using protection curve 4 in Fig. 2 is reduced to curve 2.

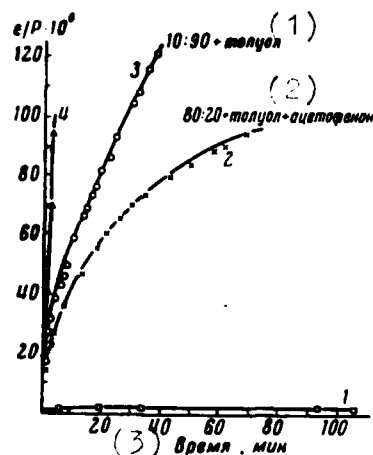


Fig. 2. Development of relative deformations ϵ , which happens per unit of stress P , dyne/cm², in the time for copolymers MMA : MA, plastified by toluene and acetophenone:

(1) (80 MMA : 20 MA) + 50% toluene (with protection from evaporation);
 (2) (80 MMA : 20 MA) + 50% toluene + 120% acetophenone (without protection);
 (3) (10 MMA : 90 MA) + 50% toluene (with protection);
 (4) (80 MMA : 20 MA) + 50% toluene + 120% acetophenone (with protection).

Key: (1) Toluene; (2) Toluene plus acetophenone; (3) Time, minutes.

There is one more system, which contains 170% of plastifier (80 MMA : 20 MA + 170% toluene) which has the same deformation curve 4, as all preceding ones.

It is interesting to note that the level of curve 1 in Fig. 2 and for the other system, the pure copolymer 10 MMA : 90 MA, is a level at which NMR signals do not occur from the polymer in the dispersion. The deformation curve 1 in Fig. 2 almost precisely coincides with the same curve for the pure copolymer (10 MMA : 90 MA), the NMR spectrum of the

37.5% dispersion of which, not indicated in Fig. 1, does not contain anything except the unique characteristic signal of water.

We express our gratitude to Ye. I. Mikhaylova for help in the experimental part of the work.

Conclusions

1. We derived NMR spectrum for 33% emulsions of copolymers of methylmethacrylate (MMA) and methylacrylate (MA) in the ratio 80 : 20 and 10 : 90 with toluene content 17% and additional introduction of acetophenone or toluene 40 parts by weight for 100 parts by weight of emulsion.

2. It was found that the spectrum of the original emulsion 80 MMA : 20 MA does not contain signals of the copolymer, but the signal does show up with an increase of mobility and, consequently, deformability of the polymer molecules due to an increase content of elastic component of MA in the copolymer (up to 90%) for plastification of dispersed particles by acetophenone and toluene in the aqueous medium.

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POLYMERIZATION OF METHYLMETHACRYLATE IN THE PRESENCE OF ALLYLCAPTAX

B. D. Saidov, A. S. Bank, M. A. Askarov, G. V. Leplyanin

A number of works have been devoted to a study of polymerization of allyl compounds and their affect on kinetic features of the transformation of vinyl monomers [1, 2]. However, there is little information in the literature on polymerization of monomers with allyl additives during chemical initiation to high degree of conversion. In this article we present a study of intense polymerization of methylmethacrylate (MMA) in a mass in a presence of allylcaptax (AK) with initiation by dinitrile of azoisobutyric acid (DAK).

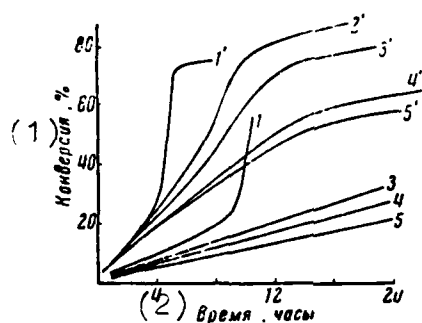


Fig. 1. Polymerization of MMA in the presence of AK with 50 (1-5) and 60° (1'-5'); 1,1' - without retardant; 2,2' - 1.44; 3,3' - 2.70; 4,4' - 4.97; 5,5' - 9.43 mole % AK.

Key: (1) Conversion; (2) Time, hours.

Experimental Part

Kinetic features of the polymerization were studied by the dilatometric method [3] at 50 and 60°; as a sealing liquid we used glycerin. MMA was repeatedly rinsed with 5-10% solution of NaOH, by water, then dried by potassium chloride and distilled with load discharging, boiling point 61°/200 mm.

AK (S-allylcaptax) was obtained by the known procedure [4] by the action of allyl bromide on an alcohol solution of potassium salt of captax; after purification it had boiling temperature 154-156°/3mm, n_D^{20} 1.6630; nitrogen content: discovered, %: 6.63, 6.83; calculated 6.75%.

Captax (benzthiazolethione-2) was recrystallized from water,

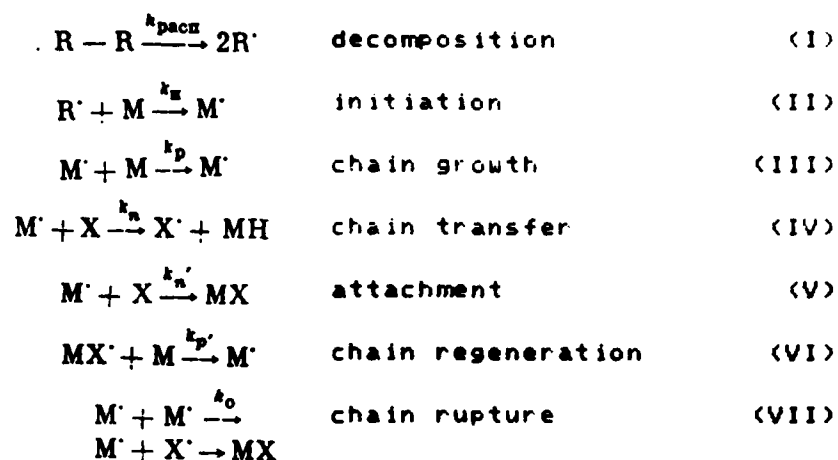
melting temperature 175° . DAK was cleansed by recrystallization from alcohol, melting temperature 103° ; amount of DAK is 2.9×10^{-3} moles/l. PMMA was twice precipitated from benzene by petroleum ester and dried in a vacuum at 25° . The molecular weight of PMMA was determined viscosimetrically according to the formula $[\eta] = 0.835 \times 10^{-4} M^{0.73}$.


Results and their Discussion

Polymerization of MMA in the presence of AK in the initial stage and with high degree of conversion precedes with considerable reduction of velocity. As is evident from Fig. 1, an increase of concentration of AK from 2.7 to 9.44 mole. % leads to a decrease in the rate of polymerization the entire segment of transformation.

Because the delay of polymerization is achieved during interaction of the allyl group with the growing end of the chain without participation of the double bond with the formation of the recombining radicals, the rate of the reaction of separation of the chain increases. The relative mobility of AK molecules during the increase of viscosity of the polymerization system leads to disappearance of the kinetic discontinuity, which corresponds to the region of the gel affect, which is characteristic for intense polymerization of MMA.

Slowing down of the polymerization process [5] of MMA can be represented in the form



Here M is MMA, X is -  -S-CH₂CH=CH₂.

From the scheme it follows that the transfer of a chain with separation of the alpha-hydrogen atom leads to the formation of a slightly active radical due to the affect of delocalization of the unpaired electron.

Earlier [6] for the system MMA - AK we found constants of the relative reaction capabilities $r_1=3.15$ and $r_2=0$; where as in the case of interaction of molecules of AK with growing ends of the chains the latter become inactive or capable of attaching only molecules of the basic monomer. This mechanism of interaction is typical for allyl monomers, which participate in the process of the degenerating transfer of a chain [7]. As a result of this the copolymers which are formed contain small number of AK links.

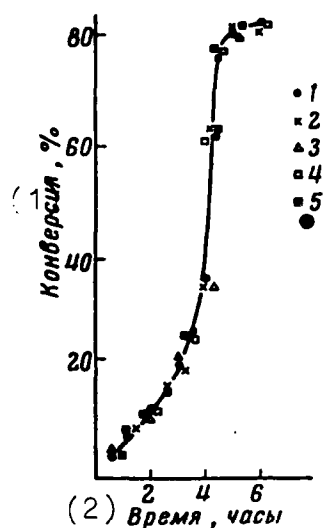


Fig. 2. Polymerization of MMA in the presence of captax at 60°.

Amount of captax (mole. %): (1) - without captax; (2) - 0.5; (3) - 1; (4) - 1.5; (5) - 2

Key: (1) Conversion; (2) Time, hours.

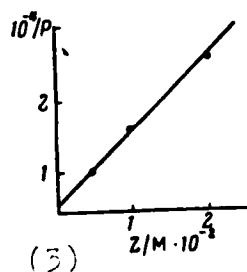


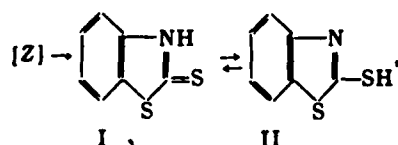
Fig. 3. Relationship of $1/P$ to the concentration $[Z]/[M]$ for initiated polymerization of MMA at 60°.

The relative inhibiting activity of the allyl group was qualitatively evaluated by comparison of kinetic features of MMA polymerization in the presence of captax.

Figure 2 represents kinetic features of polymerization of MMA in the presence of captax to high degree of conversion from which it is evident that the latter does not have an inhibiting action. By determination of the molecular weight of PMMA for small conversions in relationship to concentration of captax using Mayo's equation [2]

$$\frac{1}{P} = \frac{1}{P_0} + \frac{k_z}{k_p} \cdot \frac{[Z]}{[M]},$$

where P and P_0 are coefficients of polymerization in the presence and absence of a transfer agent of the captax chain; [Z] is the concentration of the chain transfer, [M] is the concentration of monomers; k_z is the transfer constant; k_p is the growth constant of the chain, on the slope of the direct relationship $1/P$ to $[Z]/[M]$ the transfer constant of the chain k_z/k_p was calculated, which is equal to 60 (Fig. 3). It is known that captax exists only in the thione form



which allows one to view it as a secondary amine, which participates in the chain transfer reaction [8].

Thus, the observed constancy of the rate of polymerization of MMA in the presence of AK with high degrees of transformation can be explained by the increase probability of the entry of the molecule of the retardant into the reaction of chain transfer IV, which with an increase of conversion compensates for the decrease of the k_0 chain.

Conclusion

It is shown that when there is intense polymerization of methylmethacrylate in the presence of allylcaptax the constancy of the rate of the process is due to participation of the allyl monomer in the reaction of the chain transfer. We calculated the transfer constant of the chain during polymerization of methylmethacrylate in the presence of captax.

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